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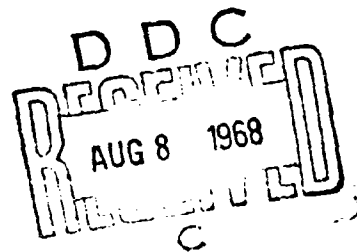
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THE BIOLOGICAL SIGNIFICANCE OF THE MECHANISMS  
OF REACTION OF GASES AND CHEMICAL AGENTS  
SUSPENDED IN AIR IN INDUSTRIAL ATMOSPHERES

[Following is a translation of an article by Dr. H. Cauer, chemical-engineering consultant, in the German-language periodical Fortschritte der biologischen Aerosol-Forschung, 1957-1961 (Progress in Biological Aerosol Research 1957-1961) pp. 275-282.]

We know from work done in mines that chemical agents suspended in air and having particle sizes with radii between approximately 0.1 and 3.0 microns are most successful in penetrating through to the lung end-passages, due to the lesser Brownian movement of such particles. Similar results were obtained in investigations on fogs during the time of World War I. Particles of this order of size were found to penetrate through the gas masks and infiltrate deeply into the lung passages. The much smaller, but much more mobile, gas particles could, instead, be much more readily captured. It is also known now that corrosion forms predominantly due to the deposition of very fine droplet condensation nuclei as moisture and very much less due to the direct action of dry, highly mobile gases. Such should also similarly be the case with smog damage to vegetation. The fine salt mist on the skins of sailors in calm weather also can be explained by the deposition of such droplets.

These facts are of general importance in considering the biological significance of air in industrial zones. This is particularly true since such air is characterized by the fact that it is pronouncedly rich in highly hygroscopic materials acting as condensation nuclei. All hygroscopic compounds of this kind, both gaseous and in the form of fine dust, form such condensation nuclei when they enter a sufficiently water-vapor-saturated environment. They coagulate in split seconds, react with one another and with gas particles, and expand as a result of the water which is taken up. Then, in accordance with thermal laws, they are deposited on relatively cool surfaces. If they are inhaled into the respiratory tract they can carry their chemical contents as far as the sensitive lung end passages and there deposit it. This brings up the decisive point as to just what is the chemical nature of such condensation nuclei, that is, of the nuclei of fogs and dust, and what has been the history of their formation and development. If, for example, they consist of chemical traces like  $\text{NO}_2$ , ammonium compounds or even only dipolar  $\text{Co}_2$  (13) found in the high mountains, they serve effectively as carriers of water in liquid form. Their chemical nature cannot be regarded as foreign or

alien to the body. If they have formed over the oceans, then the droplet nuclei will contain an appreciably higher chemical content, which will consist especially of halogen compounds and other substances of the sea (8). Neither can these be considered foreign or alien to the body. If they are produced over industrial zones, however, then their chemical nature will be complex. The substances will be predominantly foreign to the body and may possess reducing or oxidating properties. They may be acid, neutral or slightly alkaline. The most important fact is that they are able to change by reacting with one another and with gases, even when they are only a short distance away from their source. In place of fine drops of acid, neutral salts may appear, for example.

Thus comparative studies of a medium-sized ore-roasting plant outside the Ruhr (3) showed that the larger dust particle droplets in the immediate vicinity of the low-temperature furnace contained mostly reducing sulfites, while the smaller contained mostly sulfates. At a greater distance away, about 100 meters from the furnace, the ratio was reversed. Although at first the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  was 1 : 1.53, the ratio at over 100 meters away was 1 : 0.23. This illustrates how quickly sulfites or  $\text{SO}_2$  can be oxidized to sulfates or  $\text{SO}_3$ . In addition,

comparative analyses of the condensation process against the Stratmann (15) and other (10) methods of quantitative determination gave results of the same order of magnitude on converting the figures to represent comparable quantities of sulfur. Accordingly, then, the oxides of sulfur could, at the latest, have joined the nuclei of condensation after traveling 100 meters, having been dissolved in very fine droplets. The process of condensation is, therefore, sufficient even at this distance as a method of total determination when there is sufficient moisture in the air. Besides, the quick changing of  $\text{SO}_2$  into  $\text{SO}_3$

has not been sufficiently taken into account by American investigators to date. In America the amount of oxide of sulfur measured is converted into  $\text{SO}_2$  without taking into consideration the form in which it makes its appearance. In Germany, Stratmann (14) has already made mention of this fact. When dust droplets of this kind with  $\text{SO}_3$  ions

are deposited on vegetation, serious smog damage occurs if the acidity of the droplet is buffered by coagulation with high-cation particles. The damage is generally considerably greater when both sulfate and sulfite are simultaneously present and are predominantly available as free acids, such as is the case in the vicinity of sources of emission, as proven by the existence there of barren areas stripped of vegetation. If the droplets contain only buffered sulfates, such as, perhaps, calcium, iron or magnesium sulfate, the damage then may be only slight. It is, therefore, a matter of decisive importance in air-contamination investigations that one investigate the pH of the dust, its Redox-value and, no less important, the quantity of sulfite by the Stratmann test, to be able to correctly evaluate the biological significance of the industrial atmosphere. Mention must also be made in this connection of the fact that the kind of damage shown by the vegetation differs with

the type of substance deposited, and that this can be drawn upon as an indication of the character of the actual substance being deposited. This field of investigation is mentioned in the works of L. Holte (4, 5, 6 and 7).

In this connection, let us take a look at Figure 1. It shows two curves. The upper curve shows values of  $SO_4$  in the dust or in condensation nuclei just 100 meters from the smog source; the lower curve shows the pH figures taken at the same time. This picture corroborates the standard assumption that an increase in acidity or a drop in pH is accompanied by an increase in sulfuric acid content. If, by comparison, one observes the pH values and sulfate concentrations in Figure 2, it becomes clearly apparent that the relationship of high sulfate concentration to low pH does not always hold true. These readings were taken in the center of an urban area at least one kilometer from the nearest emission source. The discrepancies in pH and sulfate figures, therefore, are not interdependent. When very high sulfate figures are present, the pH may fall to the weak acidulous level. The sulfuric or sulfurous acid content of the fine dust droplets is buffered in this case by the reaction between alkaline dust particles and acid droplets.

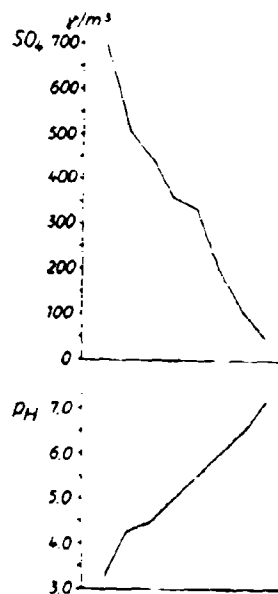
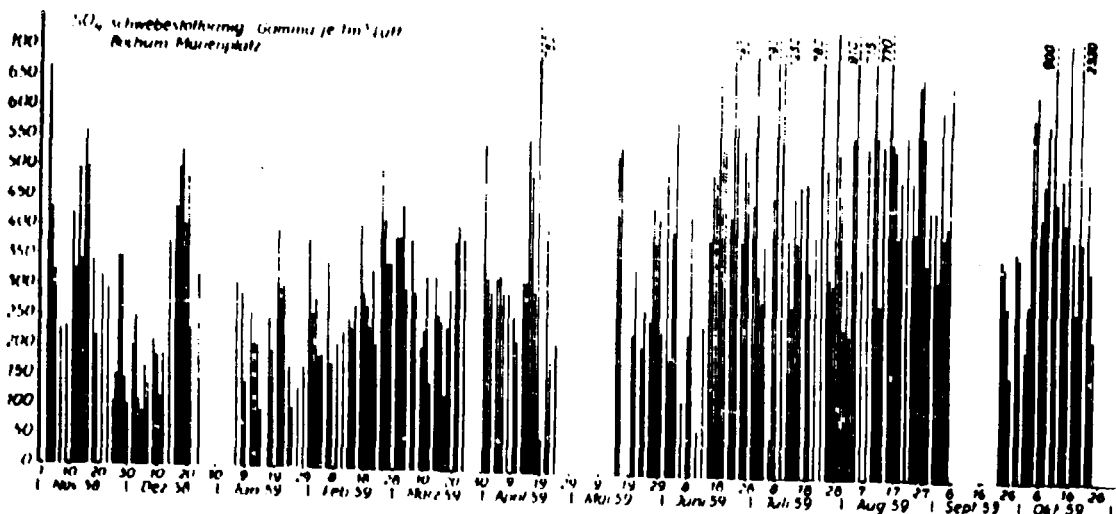


Figure 1. Drop in pH with increasing  $SO_4$ -content, measured 100 meters from the Hannibal colliery stack, Bochum, Germany, which served as the smog source.

SO<sub>4</sub> in form of chemical agents suspended in air  
(mg. per cubic meter of air) Marienplatz, Bochum



pH of the air-suspended chemical-agent droplets'  
condensate

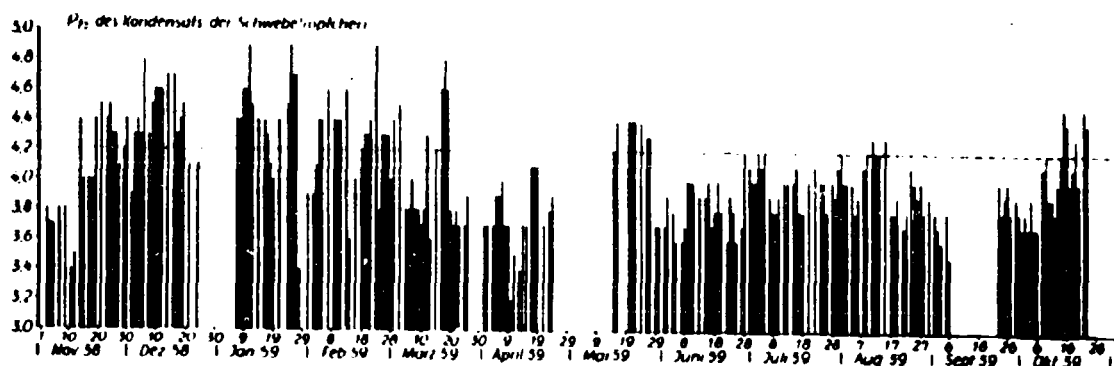


Figure 2. Example of the disproportionality between SO<sub>4</sub>-content and pH in the condensate of air-suspended chemical-agent droplets, measured at Marienplatz, Bochum.

Knowing the fact that biological and corrosion damage are caused much more by the acids present in aqueous solution in the condensation nuclei than by dry gases, and given the prerequisite that most of the gases concerned are taken up by the condensation nucleus and transformed into the water-soluble form, we should next consider the quantities of  $\text{SO}_3$  coming from  $\text{SO}_2$  gases compared with the  $\text{SO}_4$  coming from  $\text{SO}_3$  gases in the condensation nuclei droplets. First of all we should mention the fact that the Americans assume that the quantity of  $\text{SO}_2$  gas in industrial atmospheres greatly exceeds the  $\text{SO}_3$  gas content; it is, therefore, highly probable that it also exceeds the amount of sulfite in the condensation nuclei. Month-long investigations in the center of a city (Figure 3) showed only one day on which the  $\text{SO}_3$  content of the dust droplets was as high as their content in  $\text{SO}_4$ , and only three days on which the former was greater. It should be made quite clear that the oxidizing gases available in the air, and above all, also dusts, such as iron oxides, carry out their oxidizing action on the oxides of sulfur when the droplets unite in midair and can thereby considerably change the overall chemical properties of the air and the biological effects produced by it in a short time.

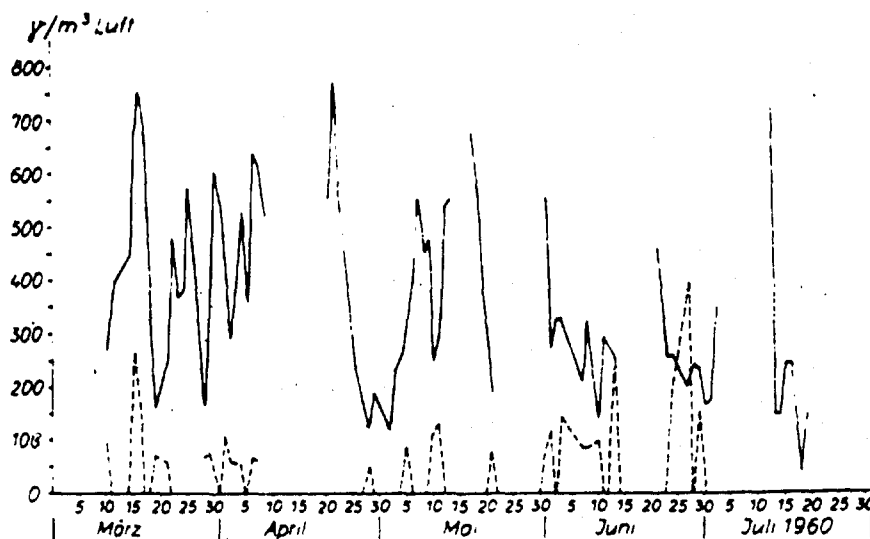


Figure 3. Determination of  $\text{SO}_3$  and  $\text{SO}_4$  contents in the condensate of chemical agents suspended in air in droplets from dust in Bochum ( $\text{SO}_4$ -ions represented by solid line;  $\text{SO}_3$ -ions by broken line. [Luft = air]).

A further example is given by the results of a thorough investigation on the grounds of a fertilizer manufacturing plant. Although there was a considerable quantity of nitrous gases escaping in the form of brown clouds from the stacks, the pH of the condensation nuclei on the grounds of the plant and also over 100 meters away [here evidently there is a line missing in the original text at the bottom of page 272] with almost no wind. This absence of free, corrosive acids in the air at ground level had not been expected. It was caused by the fact that traces of ammonia were given off to the air together with fine dolomite dust during the productive process. These two reaction partners of nitrous substances led to the formation of calcium and ammonium nitrates. The crystals of these substances could be seen drizzling down, and were picked up as very fine dust and investigated. The formation of these crystals prevented acid droplets from being formed. Acid damage to vegetation was only to be noted when, due to disturbances in the manufacturing process, there was a deficiency in substances having alkaline composition.

Mention should also be made of an example of still unproven assumption of the biological significance of metabolic processes in industrial atmospheres. It is assumed in America that there is a process of conversion of  $\text{NO}_2$  into  $\text{O}_3$  which goes on under the influence of sunlight.

Meiburger (12) in his publications is generally very cautious on this point and talks of a number of chemical mechanisms which may be possible. He makes reference to Johnston (9). According to Johnston, the high ozone readings taken in Los Angeles from smog in industrial haze are brought about by the fact that appreciable quantities of nitrous gases become rearranged to  $\text{NO} + \text{O}$  under the influence of sunlight and the oxygen atoms combine to form ozone. According to investigations which were reported to me last October in London at the convention of the Society of Bioclimatology and Biometeorology, these processes are said to take place even in the complete absence of ultra-violet radiation under a plastic dome, i.e., in the presence of wave lengths longer than Dorno-radiation. In addition, traces of nitrous oxide present as photosensitizers would permit the oxygen in the air to react with hydrocarbons and their derivatives, which leads to the formation of compounds which irritate mucous membranes. These compounds would be said to consist of ozone, organic peroxides, formaldehyde, and acrolein, among others. Now these are the very same substances, excepting the first, which are brought about by an incomplete combustion in industrial processes, even in complete darkness; the author has proven this for himself by working in submarines and elsewhere.

This fact, together with the theoretical difficulty of explaining the formation of ozone, induced me to perform suitable experiments. As is shown in Figure 4, these experiments demonstrated that on charging a glass chamber with 0.3 mg. of  $\text{NO}_2$  per cubic meter of air, 3 meg. of ozone were formed with 72 hours with complete exclusion of light. If one allows normal daylight, excluding the short-wave, ultra-violet portion, filtered through panes of glass, to operate on the same amount of nitrogen peroxide, then about 9 meg. of ozone per cubic meter of



air were found to have formed after 40 hours. It is informative to note that at first no ozone could be found during the period of darkness, but, instead, it only appeared when the  $\text{NO}_2$  had become greatly thinned out after most of it had been allowed to settle on the walls of the chamber.

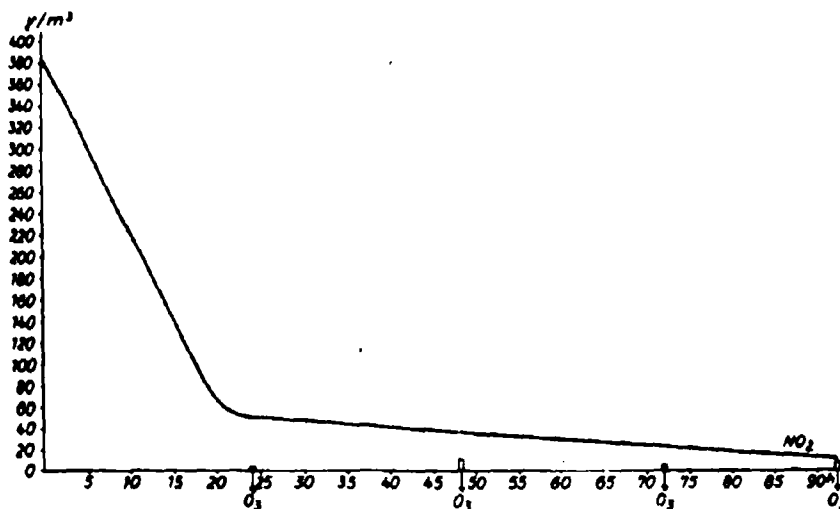


Figure 4. Formation of ozone from nitrous gases in the dark (full columns) and under the influence of daylight (empty columns). The curve drawn gives the  $\text{NO}_2$  concentration plotted against time in hours.

The drop in  $\text{NO}_2$  is steep also at the start as is shown by the curve. These experiments have not been finished yet and are to be carried on in the future. It would seem justifiable after this to point out that:

1. The assumptions of the formation of ozone from nitrous gases under the influence of daylight made by the Americans is not incorrect.
2. Ozone can be formed in small quantities from nitrous gases even in the absence of light.
3. The ozone near the ground which is increasingly pointed to in the literature (11) nowadays can in no case have originated from such processes.
4. The formation of ozone from nitrous gases is of no biological significance, either directly or indirectly.

It is also stated in many quarters that the high levels of ozone found in measurements taken at Los Angeles must be simulated by other substances. This assumption is not entirely incorrect, then, because an industrial atmosphere must be quickly reduced by reducing substances. A paper by Warabt should be expected after the talks in London in the near future.

The few examples given here should suffice to show that the mutual reactions of the different substances in the air can be of high biological significance. The air is continuously undergoing chemical and physical change so that a determination of its momentary biological significance is insufficient if based on its composition in specific substances, calculating this on the basis of a compound which may, perhaps, not even be present. Beyond this should be determined at least the direction in which the reaction is taking place, whether oxidizing or reducing, and whether acidity or alkalinity are increasing. This is now readily possible with the aid of the condensation process. Furthermore, attempts must be made through the setting up of special processes to carry out step by step a kind of total analysis of the air. The work of Strataann and Holte and utilization of the condensation process seem to the writer to be a start in this direction.

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